The Determination of the Acidity of a Tan Liquor

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ERNEST LITTLE, M.A.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE, COLUMBIA UNIVERSITY

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The Determination of the Acidity of a Tan Liquor

The determination of the acidity of a tan liquor has been a favorite problem of investigation among leather chemists during the past forty years. It is a question of very great importance due to the fact that the acidity of the liquor is one of the factors governing the rate of tanning, which in turn, determines to a very great extent the quality of leather produced.

Proctor[1] has presented data which he obtained by the use of twelve of the most important methods which had been published at that time, and as a result of his very careful work many of these methods have been definitely discarded.

The lime water method as outlined by Proctor[2] was first tried, but unsatisfactory results were obtained. Briefly, the method consists of titrating a measured amount of a clear tan liquor, preferably without dilution, with a saturated solution of lime water. The following are fair examples of the results obtained.

Liquor No.	Cc. $Ca(OH)_2$ Used	Duplicate Analysis
1	40.15	40.35
2	40.76	40.45
3	35.65	35.70
4	20.35	20.70
5	38.25	38.65

Two different analysts obtained results for the same liquor which differed by as much as 0.70 cc. Proctor commenting on his own method says "The real objection to the method lies in the uncertainty of the indicator *viz.* the insoluble calcium tannin compounds. This involves two main defects, since certain tannins give somewhat soluble lime salts, and some organic calcium salts are insoluble, and secondly, the indefiniteness of the end point." To overcome the error due to the formation of insoluble calcium salts other than the tannates, Proctor suggests that calcium chloride be added to the acid solution and filtered before titration. This suggestion is obviously poor as it would increase the concentration of calcium ion and hence hasten the precipitation of the calcium tannates. To eliminate the indefinite end point, especially in weak liquors, Proctor recom-

[1] *J. Soc. Chem. Ind.*, **29**, 1354 (1910).

[2] "Leather Industries Laboratory Book." Spon. London, 1908.

mends the addition of a neutral tanning solution to act as an indicator. If this suggestion is to be followed, enough of the tannin compound must be added to bring the total concentration to a definite value, which must be observed in each analysis, otherwise concordant results will not be obtained.

Kohnstein and Simand[3] put forth a method in which the liquor is treated with pure magnesia, only those acids forming soluble magnesium salts being determined. This method was not tried out as Proctor's results and the criticism of Bennett and Wilkinson[4] seem to prove that the method is too complicated and not sufficiently accurate to warrant its adoption.

One of the earliest methods was put forth by Koch.[5] Koch precipitated the tannins with a dilute aqueous solution of gelatin and titrated the remaining solution with tenth normal alkali. This method through its many modifications Paessler and Spanjer,[6] Reed[7] has given rise to the present official method of the American Leather Chemists Association which is discussed in much detail in a later part of this article.

Stiasny[8] suggests the use of formaldehyde in a strong hydrochloric acid solution for the precipitation of the tannins. This method has been found to work well with some liquors but is not capable of general application.

In 1906 a committee appointed by the A. L. C. A.,[9] recommended a method which detannizes by shaking a measured amount of the diluted tan liquor with moist hide powder and zinc oxide and filtering. To a portion of the filtrate a little more zinc oxide was added and titrated with $N/10$ alkali using phenolphthalein as indicator. This method was not tried out as it obviously is not good. Proctor and other investigators report that they find the method to give very low results. This is, of course, due to the neutralizing effect of the zinc oxide. Another error in the method is that the committee directs that a blank be run to determine free acid in the hide powder, assuming that it would give up as much acid to a diluted tan liquor as it does to distilled water. This faulty method of determining the blank prevented the method from giving still lower results. It has been shown by data not presented here, that the fundamental objection to this method is not the use of hide powder, but that the low results are due

[3] *Ding. Polyt. J.*, **256**, 38 (1885).
[4] *J. Soc. Chem. Ind.*, **26**, 1186 (1907).
[5] *Ding. Polyt. J.*, **265**, 33 (1887).
[6] *Collegium*, p. 10, (1903).
[7] *J. Am. Lea. Chem.*, **3**, 85 (1908).
[8] *Der Gerber*, **1905**, p. 185.
[9] *J. Am. Lea. Chem.*, **1**, 223 (1906).

to the action of the zinc oxide, while the lack of concordance is due to the method of running the blank on the hide powder, rather than to any error peculiar to the hide powder itself.

One of the most singular methods proposed for detannizing the solution is that of Simands, who recommends the use of charcoal for this purpose. It is easily understood why the results showed variations from ten to twenty per cent. when this method was used. This method in 1906 was the official method of the A. L. C. A. The report of the committee appointed to investigate it showed, in some cases, variations as high as sixteen per cent.

Hoppenstedt[10] recommends the use of an alcoholic solution of quinine for detannizing. The precipitate is filtered and a portion of the filtrate titrated with $N/10$ alkali using phenolphthalein as an indicator. This method was tried out but most unsatisfactory end points were obtained and the results were not at all concordant. Proctor[11] suggests a slight modification of this method which he shows gives better results. A committee of the A. L. C. A.,[12] reported this method as being the best of the methods then in use.

Reed[13] published a modification of the Koch method. Due to much careful and painstaking effort on the part of Reed, a modification of this method has been accepted as the official method of the A. L. C. A.

Phelan and Fiske[14] suggest that the acidity of a tan liquor be determined by the amount of carbon dioxide evolved when a measured amount of tan liquor is treated with an excess of calcium carbonate. The difficulties of manipulation of the method employed for the determination of carbon dioxide in general are well known, and although the authors have used a specially modified apparatus it is hardly applicable as a control method.

Yocum[15] recommends the use of gum arabic with gelatin as a method of detannizing. This method makes no special contribution and has been generally discarded.

Sand and Law[16,17] published an electrometric method for the estimation of the acidity of tan liquors. The apparatus used in their work is practically the same as the well known set up employed by

[10] *J. Am. Lea. Chem.*, **2**, 301 (1907).
[11] *J. Soc. Chem. Ind.*, **29**, 1354 (1910).
[12] *J. Am. Lea. Chem.*, **1**, 223 (1906).
[13] *Ibid.*, **3**, 85, 1908).
[14] *Ibid.*, **3**, 99 (1908).
[15] *Ibid.*, **5**, 292 (1910).
[16] *J. Soc. Chem. Ind.*, **6**, 52 (1911).
[17] *Ibid.*, **6**, 428 (1911).

Hildebrand.[18] Sand and Law used a hydrogen electrode very similar to Hildebrand's, together with a normal calomel cell, containing 3.5 N potassium chloride in the arm which makes contact with the solution being titrated. The potential difference existing between the calomel cell and the hydrogen electrode was measured by balancing it against a fractional part of the current furnished by a dry cell the latter being regulated through the agency of a sliding rheostat. The point of no flow of current in the circuit was determined by the use of a capillary electrometer and the potential difference necessary to balance that existing between the hydrogen electrode and calomel cell was measured by the use of a delicate milli-voltmeter, which was frequently checked against a standard Weston cell. A voltage of 0.69 volt was chosen as the end point as this is the voltage obtained by running $N/10$ sodium hydroxide into $N/10$ acetic acid until the faintest pink color of phenolphthalein appears. By use of this set up $N/10$ sodium hydroxide was run into diluted tan liquors until the end point was reached, then measured amounts of $N/10$ organic acids were added and $N/10$ sodium hydroxide again run in until the end voltage was obtained the second time. The second addition of $N/10$ alkali added agreed in every case with the amount of $N/10$ acid which had been added. The organic acids had previously been standardized against $N/10$ NaOH using phenolphthalein as an indicator.

Neutralization curves for three tan liquors were also given. The curves show that the change in conc. H^+ per unit of alkali added is too small to allow of a satisfactory titration by the use of indicators.

Bennett[19] publishes a method in which he divides the acids present in tan liquors into three groups (*a*) "The tannic acids" (*b*) the volatile acids (*c*) the non-tan and non-volatile acids. He outlines a method which, when used in conjunction with the analysis of the liquors for tans by his own modification of the hide powder method, gives the above information without complicated apparatus or manipulation.

Atkin and Thompson[20] have published a very ingenious method in which they make use of a comparator designed by Cole and Onslow ("Practical Physiological Chemistry")to determine the conc. H^+ of the liquor and the amount of standard alkali or acid necessary to bring the liquor to the definite conc. H^+ that may be desired. They set the range of acidity as from pH 2.8 the highest acidity likely to be found in tan liquors to pH 4.6, the isoelectric point of gelatin.

[18] *J. Am. Chem. Soc.*, **35**, 847 (1913).
[19] *Collegium*, May, p. 106–113 (1916).
[20] *J. S. L. T. C.*, **4**, 143 (1920).

Thomas[21] gives 10^{-5} as the isoelectric point of hide protein which agrees with the plumping limit set by Proctor and Jones.[22]

Wilson and Gallun,[23] in studying the plumping of calf skins at different pH values found a minimum point at 5.1 and another at 7.6. This they interpret as indicating isoelectric points of two different forms of calf skin protein found in the purified hide.

The present official method of the A. L. C. A.[24] for the determination of the acidity of tan liquors is as follows.

Reagents.—(*a*) One per cent. solution of gelatin, neutral to hematine. The addition of 25 cc. of 95% alcohol is recommended to prevent frothing.

(*b*) A 0.5% solution of hematine in cold neutral 95% alcohol.

(*c*) Acid washed kaolin free from soluble matters.

(*d*) $N/10$ sodium hydroxide solution.

Method.—To 25 cc. of liquor in a cylinder that can be stoppered add 50 cc. of the gelatin solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least fifteen minutes, remove 30 cc. of the supernatant liquid, dilute with 50 cc. water and titrate with $N/10$ sodium hydroxide, using hematine as an indicator. Due to the prominence of this method it was studied in great detail.

The gelatin is added to precipitate the tannins as their color interferes seriously with an indicator change. The kaolin is added to assist in clarifying the solution and enable the tanno-gelatin precipitate to settle out more quickly.

A study of the action of the kaolin was first taken up. Fifteen grams of kaolin would of course possess a very large surface and suggests at once the probability of adsorption of a portion of the acids present, thus reducing the concentration of the acids in the liquor and giving low results. In order to determine whether or not this adsorption will take place the following experimental work was carried out with different normalities of sulphuric, hydrochloric, formic, acetic, lactic and butyric acids. These acids were chosen in view of the fact that the work of A. Seymour Jones,[25] in working on the natural acids of tan liquors shows that acetic, propionic, butyric and lactic acids constitute the effective portion of the natural acids found in a normal tan liquor. In some tanneries small amounts of sulphuric acid are added to "sharpen" the tan liquor.

[21] *J. Ind. Eng. Chem.*, **14**, 294 (1922).
[22] *J. Am. Lea. Chem.*, **6**, 441 (1911).
[23] *J. Ind. Eng. Chem.*, **15**, 71 (1923).
[24] Bulletin of Official Methods of A. L. C. A. (1922).
[25] Tanner's Year Book, (1911).

Fifteen grams of kaolin were added to one hundred cubic centimeters of the standard acid in a 250 cc. glass stoppered flask and put in a constant temperature bath at 18° C. The flask was shaken at short intervals during the first four hours and then allowed to remain in the bath for twenty hours. The clear supernatant solution was then decanted through a small filter paper into a burette which was thoroughly rinsed with the first portion of the filtrate. Twenty-five cubic centimeters were now run from this burette and titrated against standard sodium hydroxide using phenolphthalein as an indicator and the difference in the concentration of the solution and its original concentration determined. The results obtained are tabulated below.

HYDROCHLORIC ACID

Original Normality	Normality at Equilibrium	Per cent. Adsorbed
0.1863	0.1832	1.66
0.0878	0.0852	2.96
0.0499	0.0480	3.81
0.0091	0.0078	14.29

ACETIC ACID

Original Normality	Normality at Equilibrium	Per cent. Adsorbed
0.1810	0.1794	0.88
0.0965	0.0954	1.14
0.0465	0.0451	3.01
0.0101	0.0095	5.94

LACTIC ACID

Original Normality	Normality at Equilibrium	Per cent. Adsorbed
0.1820	0.1800	1.09
0.1083	0.1067	1.48
0.0467	0.0449	3.65
0.0090	0.0080	11.11

No special precautions were taken in the above work to insure uniformity in the samples of Kaolin used. The Kaolin was weighed out in the condition as received, just as it is used in the laboratory from which it was obtained. With sulphuric, butyric and formic acids special precautions were observed to obtain as nearly as possible very accurate results. The kaolin was run through a two hundred mesh sieve and then shaken for one-half hour in a large wide mouth bottle to insure uniformity of the sample. Exactly fifteen gram samples were weighed out and the temperature was maintained constant to within 0.05° C. The three acids so treated were chosen as they seemed to be especially representative acids; formic acid being the strongest organic acid, butyric acid an organic acid of ordinary

strength while sulphuric acid is the mineral acid which is always used. The results obtained with these acids are given below.

FORMIC ACID

I	II	III	IV	V
Orig. Normality	Normality at Equilibrium	Per cent Adsorbed	Grams of Formic Acid Adsorbed from 50 Cc. by 15 Gm. Kaolin × 10,000	Log. of Values in Table IV
(*a*) 0.09620	0.09430	1.98	43.7000	1.6405
(*b*) 0.04850	0.04690	3.30	36.8000	1.5658
(*c*) 0.02420	0.02310	4.55	25.3000	1.4031
(*d*) 0.01110	0.01030	7.21	18.4000	1.2648

VI	VII
Grams of Formic Acid Left in 50 Cc. × 100	Log. of Values Given in Table VI
(*a*) 21.6900	1.3363
(*b*) 10.7900	1.0330
(*c*) 5.3130	0.7253
(*d*) 2.3690	0.3742

BUTYRIC ACID

I	II	III	IV	V
Original Normality	Normality at Equilibrium	Per cent Adsorbed	Grams of Butyric Acid Adsorbed From 50 Cc. by 15 Gm. Kaolin × 10,000	Log. of Values in Table IV
0.17680	0.17500	1.02	73.8000	1.8681
0.09620	0.09480	1.46	57.4000	1.7562
0.04540	0.04440	2.20	41.0000	1.6128
0.0094	0.0089	5.32	20.5000	1.3118

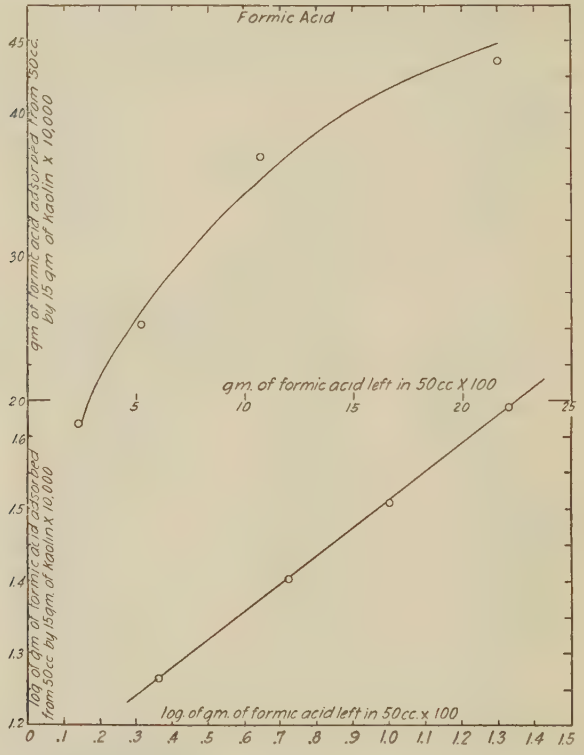
VI	VII
Grams of Butyric Acid Left in 50 Cc. × 100	Log of Values Given in Table VI
71.7500	1.8558
38.8680	1.5895
18.2040	1.2606
3.6490	0.5610

SULPHURIC ACID

I	II	III	IV	V
Original Normality	Normality at Equilibrium	Per cent Adsorbed	Grams of Sulphuric Acid Adsorbed From 50 Cc. by 15 Gm. Kaolin × 10,000	Log of Values in Table IV
0.18450	0.18130	1.73	78.4000	1.8943
0.09860	0.09590	2.73	66.1500	1.8205
0.04630	0.04400	4.97	56.3500	1.7509
0.0108	0.0091	15.74	41.6500	1.6195

VI	VII
Grams of Sulphuric Acid Left in 50 Cc. × 100	Log of Values Given in Table VI
44.4185	1.6476
23.4965	1.3711
10.7800	1.0326
2.2295	0.3483

The results for the six acids given above, show that for a $0.01\,N$ solution an average of 10.03% of the total amount of acids present was taken out of solution by the kaolin and for a $0.02\,N$ solution, as would usually be present during a titration according to the official method, the error due to the kaolin would amount to about 3.5%. A blank was run on the acid, with no kaolin present, for twenty-four hours, and no decrease in the strength of the acid resulted. Also a blank was run on a fifteen gram sample of kaolin in 100 cc. of distilled

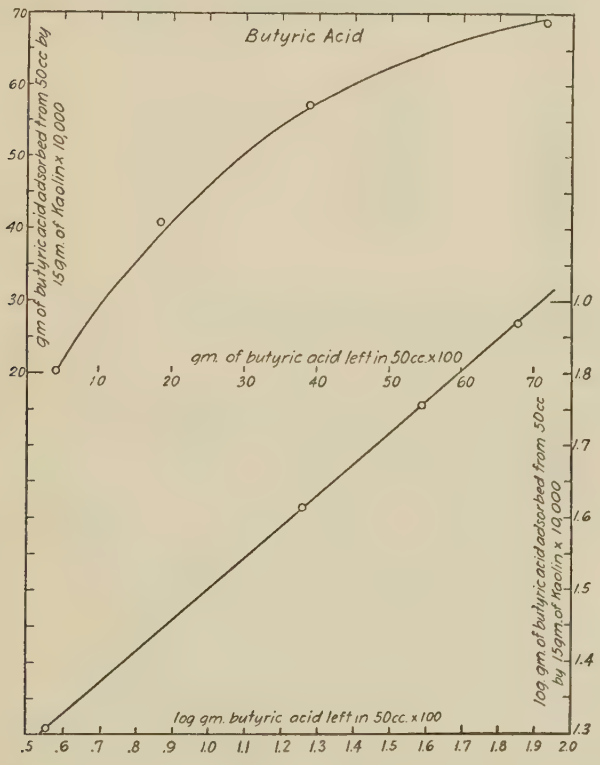


water for the same length of time and the resultant solution showed the pink color of phenolphthalein when one drop of $N/10$ NaOH was added.

The equilibrium concentrations of sulphuric, formic and butyric acids remaining in the solution were plotted against the moles of acid adsorbed by the fifteen grams of kaolin for each concentration as were also the logarithms of these values, to determine whether the first curve would approximate a parabola and the second a straight line. The graphs of these results are shown on pages 10, 11 and 12.

As the above experiments were carried out in solutions where

the conditions were not identical with those in a solution of a tan liquor which is being analyzed, according to the official method, it was thought best to determine whether the amount of acids adsorbed would be the same in both cases. Several tan liquors were, therefore, analyzed according to the official method, a 25 cc. aliquot being titrated. After the addition of kaolin, the solution was allowed to stand over night and instead of using the unreliable hematine indicator, the titration was carried out electrometrically, a pH of seven


Butyric Acid
gm. of butyric acid adsorbed from 50cc by 1.5 gm. of Kaolin x 10,000
gm. of butyric acid left in 50cc x 100
log gm. butyric acid left in 50cc. x 100
log gm. of butyric acid adsorbed from 50cc by 1.5 gm. of Kaolin x 10,000

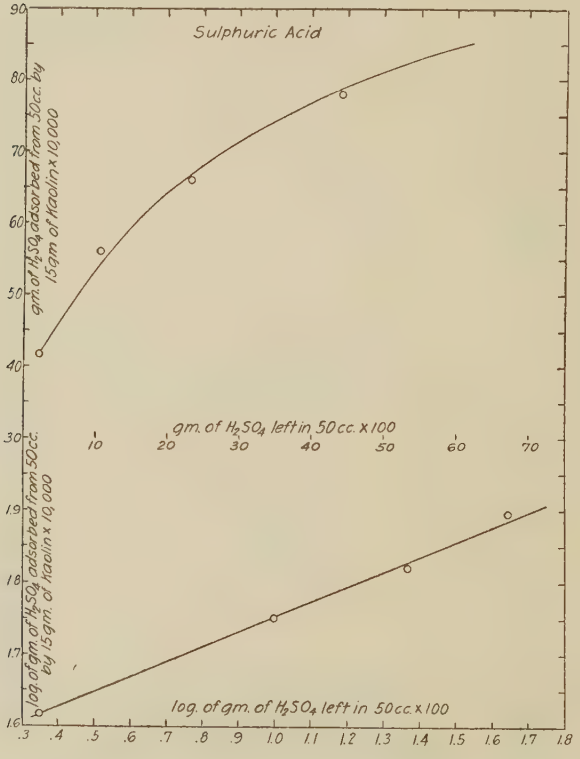
being chosen as the end point value. The results for three of the liquors follow.

	Cc. 0.02410 *N* NaOH
Liquor No. 1	11.20
Liquor No. 2	9.00
Liquor No. 3	10.20

The analysis of these same liquors was then repeated as above except that no kaolin was added. After settling over night, the clear supernatant liquid was very carefully poured into a small dry Büchner funnel, the first part of the filtrate being returned

through the filter several times and eventually discarded. The filtration was then continued, using very gentle suction. Twenty-five cubic centimeters of this solution were titrated and the following results obtained.

	Cc. 0.02410 *N* NaOH
Liquor No. 1	12.10
Liquor No. 2	9.70
Liquor No. 3	11.25


Sulphuric Acid
gm. of H_2SO_4 adsorbed from 50cc. by 1.5 gm. of Kaolin x 10,000
gm. of H_2SO_4 left in 50 cc. x 100
log. of gm. of H_2SO_4 adsorbed from 50cc. by 1.5 gm. of Kaolin x 10,000
log. of gm. of H_2SO_4 left in 50 cc. x 100

It is shown by the above data that the acidity of a tan liquor is decreased by the addition of fifteen grams of kaolin in about the same proportion as was the acidity of the organic acids previously determined and that the different conditions existing in the two solutions probably have no effect on the adsorption of acids by the kaolin.

The kaolin used in the above work was obtained from one of the largest and most reliable leather laboratories in the country. It contained practically no water soluble material and was neutral to phenolphthalein.

A portion of this kaolin was acid washed with normal sulphuric and another with normal acetic acid as follows. The sample was shaken frequently with two liters of the acid and allowed to stand over night. The clear solution was then siphoned off, two liters of distilled water added and again allowed to stand over night. This washing by decantation was repeated twenty times. This kaolin was spread out on unbleached muslin and allowed to dry at room temperature. The dry kaolin was then ground very fine and experiments were run with the $N/10$ acids as had been done with the non acid washed kaolin. The results follow for the sulphuric acid washed kaolin.

Acid	Original Normality	Normality at Equilibrium	Per cent Adsorbed
H_2SO_4	0.0986	0.0961	2.54
HCl	0.0878	0.0854	2.73
HCOOH	0.0962	0.0947	1.56
CH_3COOH	0.0965	0.0956	0.93
C_3H_7COOH	0.0961	0.0950	1.14
$C_2H_4OHCOOH$	0.1083	0.1069	1.29

With the acetic acid washed kaolin the results agreed, within experimental error, with those obtained with the non acid washed kaolin.

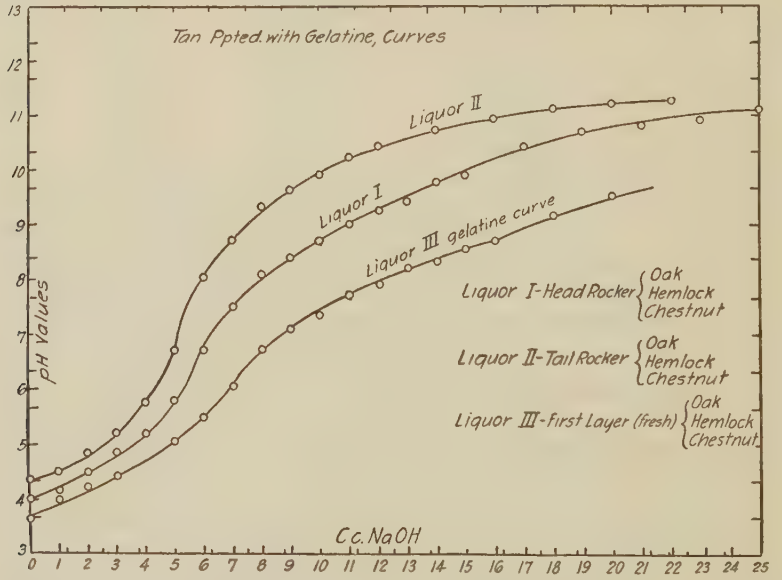
Frey,[26] as a result of his study of the action of six different samples of kaolin toward 0.02 molar acetic acid gives data which shows that in each case the acid washed kaolin takes up as much acid as the unwashed kaolin. Frey added fifteen grams of kaolin to 250 cc. of 0.02 N acetic acid, shook the solution well, then allowed it to stand for one hour, when 50 cc. were pipetted off and titrated. For the six samples which he used, he found that an average of 5.80% of the total amount of acid present was taken up by the kaolin.

The results given above show that: (1) Kaolin removes acid from solutions of those acids which occur in the tan liquors. (2) The amount of acid taken up by the kaolin varies with the equilibrium concentration in solution in the manner $\frac{x}{m} = ac^{1/n}$ as shown by the parabolic nature of the curve, and by the straight line given by the logarithmic form of the equation $\log x - \log m = \log a + {}^{1}/_{n} \log c$ and (3) Kaolin which has been acid washed and then washed with distilled water to remove the excess acid will still adsorb acid from solutions of weak organic acids. It would seem therefore, that kaolin cannot be used as in the official method without introducing an error, and that that error is definitely due to adsorption.

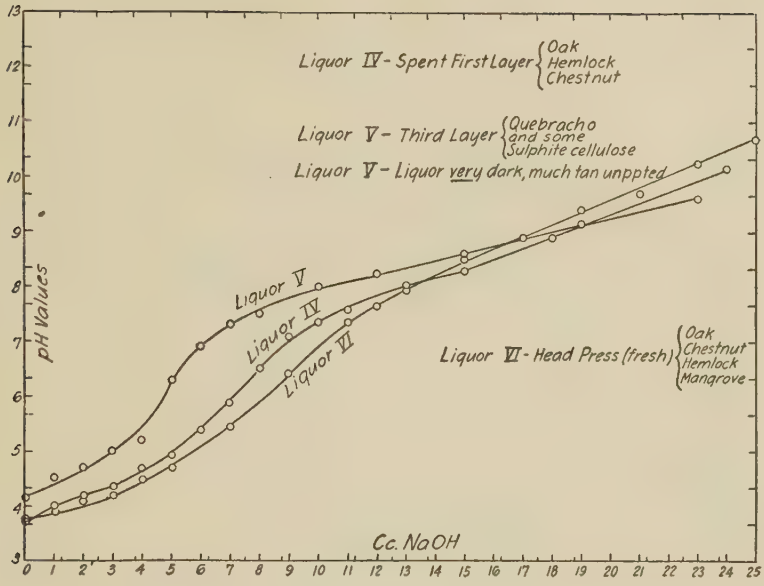
The next part of the method to be studied was the precipitation of the tans with gelatin. As the only specification of the official,

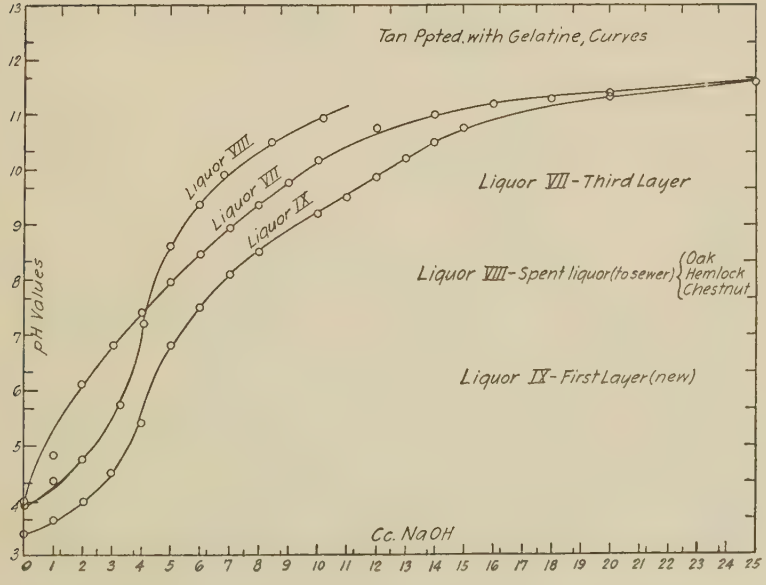
[26] *J. Am. Lea. Chem.*, **14**, 393 (1919).

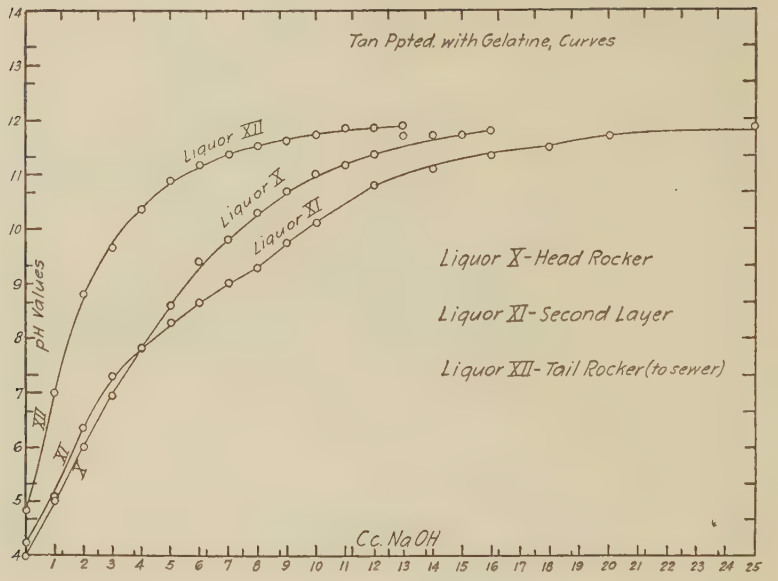
method is that the gelatin solution should be neutral to hematine, isoelectric gelatin was not used, but a large sample of J. T. Baker Chemical Company's gelatin powder, lot number 91,620 was secured and used in the following experiments. A one per cent. solution of this gelatin containing 25 cc. of ethyl alcohol per liter was made up and with it the official method for the determination of the acidity of a tan liquor was carried out, except that the total volume was made up to 300 cc. instead of 250 cc. and 50 cc. aliquots were titrated. The titration was carried out in a solution containing a Hildebrand type of hydrogen electrode which was coated with platinum black and bathed with hydrogen. The hydrogen had been purified by being passed through alkaline permanganate, alkaline pyrogallate, water,

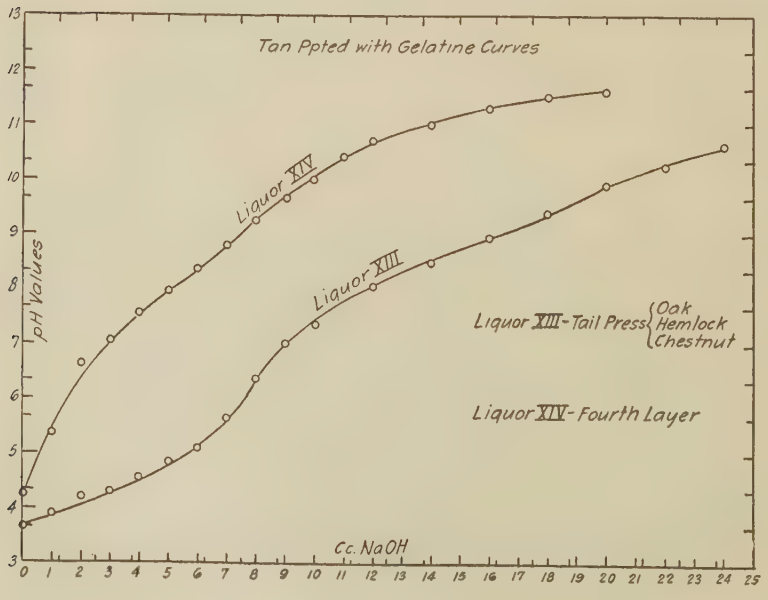


glass wool, and finally through a diluted tan liquor. A type K Leeds and Northrup potentiometer was used in the set up together with a Leeds and Northrup No. 2285 high sensitivity galvanometer, a standard Weston cell and a calomel cell with appropriate salt bridge containing a saturated solution of potassium chloride. The mercury used in the calomel cell was specially purified, having been distilled under reduced pressure, according to Hulet. The potassium chloride was carefully recrystallized and the calomel made by adding an excess of purified mercury to slightly diluted, redistilled nitric acid. After the action had continued for some time the nitric acid and remaining mercury were poured into about 300 cc. distilled water. A twenty per cent. solution of hydrochloric acid was now distilled and


Liquor IV - Spent First Layer {Oak Hemlock Chestnut
Liquor V - Third Layer {Quebracho and some Sulphite cellulose
Liquor V - Liquor very dark, much tan unppted
Liquor V
Liquor IV
Liquor VI
Liquor VI - Head Press (fresh) {Oak Chestnut Hemlock Mangrove
pH Values
Cc. NaOH

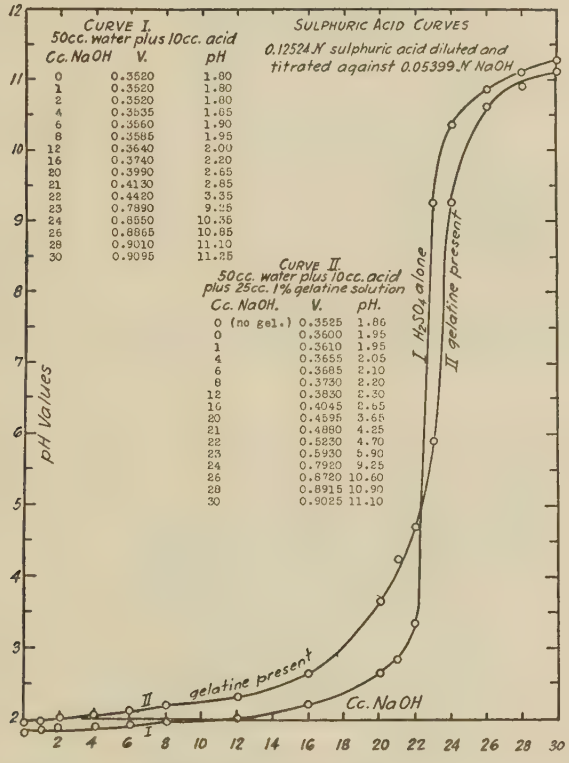

Tan Ppted. with Gelatine, Curves
Liquor VIII
Liquor VII
Liquor IX
Liquor VII - Third Layer
Liquor VIII - Spent liquor (to sewer) {Oak Hemlock Chestnut
Liquor IX - First Layer (new)
pH Values
Cc. NaOH


Tan Ppted. with Gelatine, Curves
Liquor XII
Liquor X
Liquor XI
Liquor X-Head Rocker
Liquor XI-Second Layer
Liquor XII-Tail Rocker(to sewer)
pH Values
Cc. NaOH


Tan Ppted with Gelatine Curves
Liquor XIV
Liquor XIII
Liquor XIII-Tail Press {Oak Hemlock Chestnut}
Liquor XIV-Fourth Layer
pH Values
Cc. NaOH

the middle portion of the distillate was added to the acid mercurous nitrate solution until precipitation was complete. The precipitated mercurous chloride was washed repeatedly by decantation with very pure distilled water. This especially prepared calomel was kept suspended in pure distilled water in the presence of some mercury.

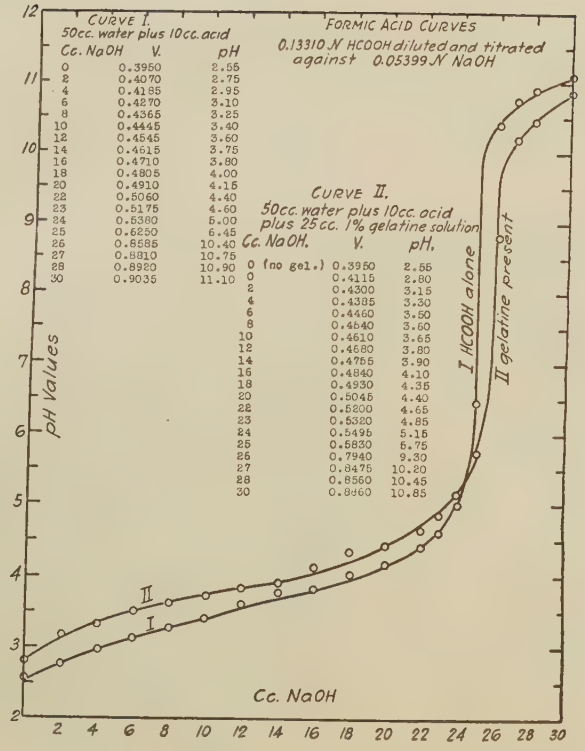
The titrations were run at 25° C. the temperature remaining constant to within 0.05° C. The titration beaker as well as the lower part of the calomel cell and salt bridge were immersed in an elec-

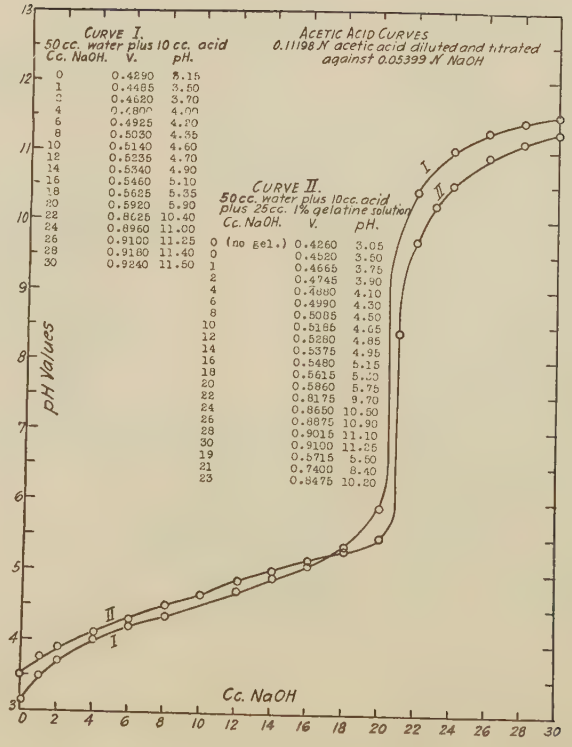


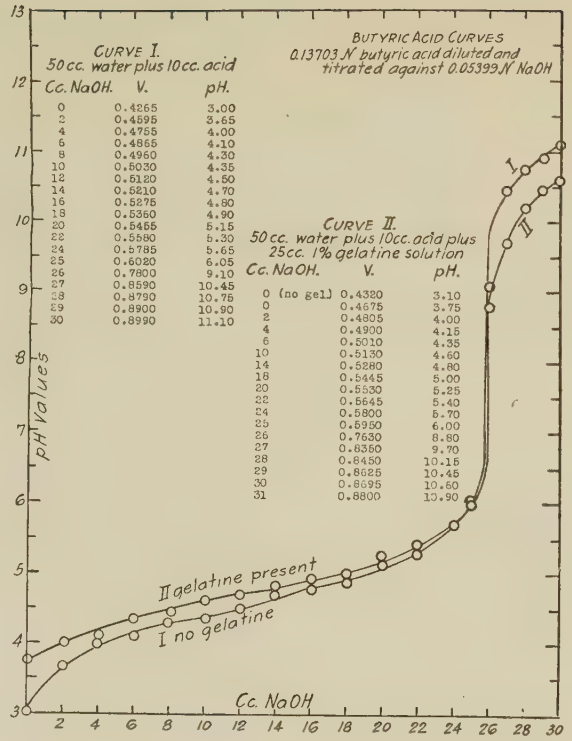
trically heated and controlled water bath which was thoroughly stirred.

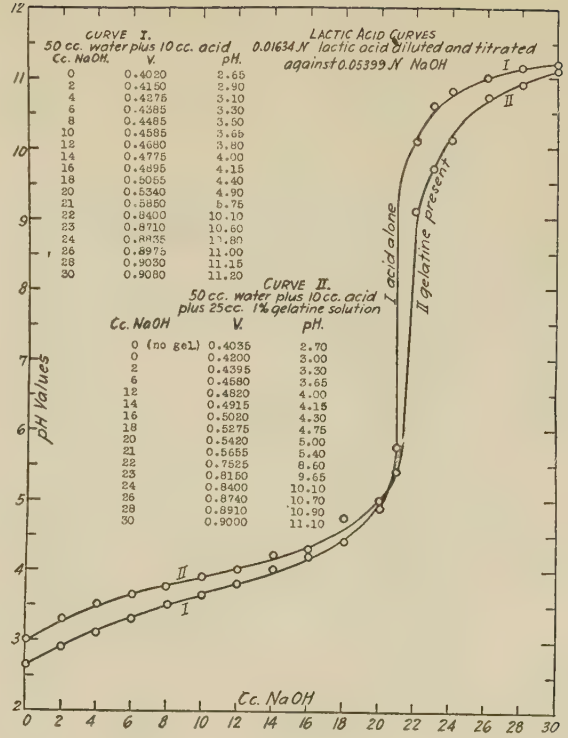
With this set up electrometric titrations were run. The voltages corresponding to certain additions of alkali were recorded and the corresponding pH values calculated by use of the Nernst formula. These pH values were then plotted against the corresponding cubic centimeters of alkali added and the titration curves shown on pages 14, 15 and 16 were developed.

The liquors used in developing these curves were analyzed according to the official method and the results on page 20 obtained.


FORMIC ACID CURVES
0.13310 N HCOOH diluted and titrated against 0.05399 N NaOH
CURVE I.
50cc. water plus 10cc. acid
Cc. NaOH V. pH
0 0.3950 2.55
2 0.4070 2.75
4 0.4185 2.95
6 0.4270 3.10
8 0.4365 3.25
10 0.4445 3.40
12 0.4545 3.60
14 0.4615 3.75
16 0.4710 3.80
18 0.4805 4.00
20 0.4910 4.15
22 0.5060 4.40
23 0.5175 4.60
24 0.5380 5.00
25 0.6290 6.45
26 0.8585 10.40
27 0.8810 10.75
28 0.8920 10.90
30 0.9035 11.10
CURVE II.
50cc. water plus 10cc. acid
plus 25cc. 1% gelatine solution
Cc. NaOH. V. pH.
0 (no gel.) 0.3950 2.55
0 0.4115 2.80
2 0.4300 3.15
4 0.4385 3.30
6 0.4460 3.50
8 0.4640 3.60
10 0.4610 3.65
12 0.4680 3.80
14 0.4755 3.90
15 0.4840 4.10
18 0.4930 4.35
20 0.5045 4.40
22 0.5200 4.65
23 0.5320 4.85
24 0.5495 5.15
25 0.5830 5.75
26 0.7940 9.30
27 0.8475 10.20
28 0.8560 10.45
30 0.8660 10.85
I HCOOH alone
II gelatine present
pH Values
Cc. NaOH
II
I


ACETIC ACID CURVES
0.11198 N acetic acid diluted and titrated against 0.05399 N NaOH
CURVE I.
50cc. water plus 10 cc. acid
Cc. NaOH. V. pH.
0 0.4290 3.15
1 0.4485 3.50
2 0.4620 3.70
4 0.4805 4.00
6 0.4925 4.20
8 0.5030 4.35
10 0.5140 4.60
12 0.5235 4.70
14 0.5340 4.90
16 0.5460 5.10
18 0.5625 5.35
20 0.5920 5.90
22 0.8625 10.40
24 0.8960 11.00
26 0.9100 11.25
28 0.9180 11.40
30 0.9240 11.50
CURVE II.
50cc. water plus 10cc. acid
plus 25cc. 1% gelatine solution
Cc. NaOH. V. pH.
0 (no gel.) 0.4260 3.05
0 0.4520 3.50
1 0.4665 3.75
2 0.4745 3.90
4 0.4880 4.10
6 0.4990 4.30
8 0.5085 4.50
10 0.5185 4.65
12 0.5280 4.85
14 0.5375 4.95
16 0.5480 5.15
18 0.5615 5.20
20 0.5860 5.75
22 0.8175 9.70
24 0.8650 10.50
26 0.8875 10.90
28 0.9015 11.10
30 0.9100 11.25
19 0.5715 5.50
21 0.7400 8.40
23 0.8475 10.20
pH Values
Cc. NaOH
II
I


BUTYRIC ACID CURVES
0.13703 N butyric acid diluted and titrated against 0.05399 N NaOH
CURVE I.
50 cc. water plus 10 cc. acid
Cc. NaOH. V. pH.
0 0.4265 3.00
2 0.4595 3.65
4 0.4755 4.00
6 0.4865 4.10
8 0.4960 4.30
10 0.5030 4.35
12 0.5120 4.50
14 0.5210 4.70
16 0.5275 4.80
18 0.5360 4.90
20 0.5455 5.15
22 0.5580 5.30
24 0.5785 5.65
25 0.6020 6.05
26 0.7800 9.10
27 0.8590 10.45
28 0.8790 10.75
29 0.8900 10.90
30 0.8990 11.10
CURVE II.
50 cc. water plus 10cc. acid plus 25cc. 1% gelatine solution
Cc. NaOH. V. pH.
0 (no gel) 0.4320 3.10
0 0.4675 3.75
2 0.4805 4.00
4 0.4900 4.15
6 0.5010 4.35
10 0.5130 4.60
14 0.5280 4.80
18 0.5445 5.00
20 0.5530 5.25
22 0.5645 5.40
24 0.5800 5.70
25 0.5950 6.00
26 0.7630 8.80
27 0.8350 9.70
28 0.8450 10.15
29 0.8625 10.45
30 0.8695 10.60
31 0.8800 10.90
II gelatine present
I no gelatine
pH values
Cc. NaOH


LACTIC ACID CURVES
0.01634 N lactic acid diluted and titrated against 0.05399 N NaOH
CURVE I.
50 cc. water plus 10 cc. acid
Cc. NaOH. V. pH.
0 0.4020 2.65
2 0.4150 2.90
4 0.4275 3.10
6 0.4385 3.30
8 0.4485 3.50
10 0.4585 3.65
12 0.4680 3.80
14 0.4775 4.00
16 0.4895 4.15
18 0.5055 4.40
20 0.5340 4.90
21 0.5850 5.75
22 0.8400 10.10
23 0.8710 10.60
24 0.8835 10.80
26 0.8975 11.00
28 0.9030 11.15
30 0.9080 11.20
CURVE II.
50 cc. water plus 10 cc. acid plus 25 cc. 1% gelatine solution
Cc. NaOH V. pH.
0 (no gel) 0.4035 2.70
0 0.4200 3.00
2 0.4395 3.30
6 0.4580 3.65
12 0.4820 4.00
14 0.4915 4.15
16 0.5020 4.30
18 0.5275 4.75
20 0.5420 5.00
21 0.5655 5.40
22 0.7525 8.60
23 0.8150 9.65
24 0.8400 10.10
26 0.8740 10.70
28 0.8910 10.90
30 0.9000 11.10
I acid alone
II gelatine present
pH Values
Cc. NaOH

Liquor No.	1	2	3	4	5	6	7	8	9
Total Solids	7.25	4.55	10.00	9.80	12.80	9.60	11.56	3.45	10.01
Soluble Solids	7.00	4.50	9.45	9.00	12.45	8.85	10.06	3.36	9.41
Tans	3.15	1.25	5.00	4.60	8.50	4.55	6.49	.80	5.14
Non-tans	3.85	3.25	4.45	4.40	3.95	4.30	3.57	2.56	4.27

An inspection of the curves given herewith shows in practically every case a peculiar flattening from a pH value of about seven to ten. It was at first thought that this effect was due to the presence of gelatin salts of the various organic acids and their titration by sodium hydroxide to sodium gelatinate. In order to substantiate this point, titration curves were developed for sulphuric, acetic, butyric and lactic acids. The titration curves for these acids in the presence of 25 cc. of a one per cent. solution of gelatin, neutral to hematine, were also developed in order to see if the peculiar flattening effect from pH values seven to ten would appear. The curves obtained are shown on pages 17, 18 and 19, the two curves being plotted together so that they may be more easily compared.

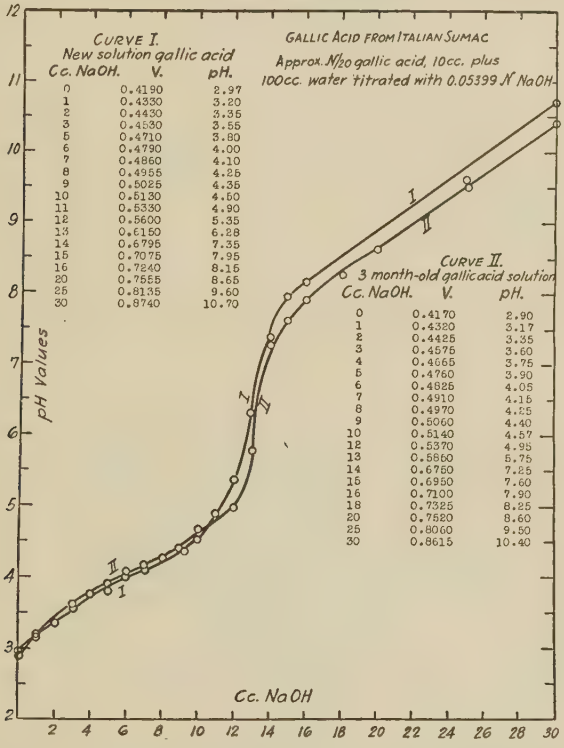
It is noticed that no such flattening of the curve, as was observed with the gelatin detannized liquors, is shown by any of these curves. It would seem, therefore, that the gelatin itself is not responsible for this effect.

The next supposition to be worked upon was that the flattening of the curve and hence the absence of a definite break was due to the presence of unprecipitated tannins. The fact that those solutions which were the yellowest and darkened most when titrated, gave curves more nearly approximating a straight line made this a reasonable assumption. In order to get some data on this point titration curves for (*a*) gallic acid (*b*) gallic acid in the presence of gelatine (*c*) pyrogallic acid (*d*) tannic acid (*e*) tan liquors with the tannins unprecipitated (*f*) these same tan liquors with tannins precipitated with gelatin were developed. The results are shown on pages 21, 22, 23 and 24.

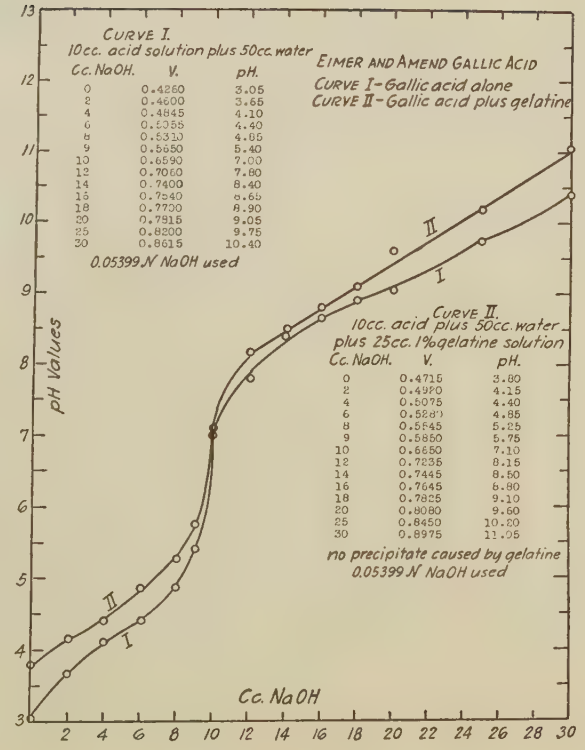
A study of these curves furnishes much interesting information. It is quite evident on the gallic acid curve that the carboxyl group was completely neutralized when a volume of 9.5 cc. NaOH had been added, resulting in a rather sharp decrease in the conc. H^+ and that the flattening of the curve from there up is due to the reaction of the sodium hydroxide with the phenolic hydroxyl groups. The pyrogallic acid curve is, as would be expected, more nearly a straight line, the sodium hydroxide reacting only with the weakly acid phenolic groups. The curve presented above, however, would indicate that the sample still contained a little gallic acid as about 1.5 cc. of $N/20$ NaOH seems to have been used up in neutralizing the carboxyl group before the more gradual neutralization of the hydroxyl

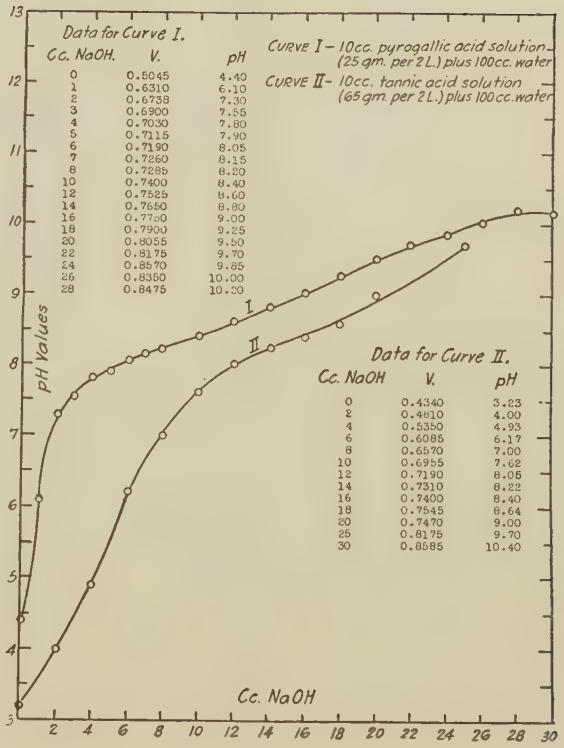
groups sets in. The tannic acid curve gives a much poorer break indicating that the properties of the carboxyl group are not as dominant as in the case of the gallic acid.

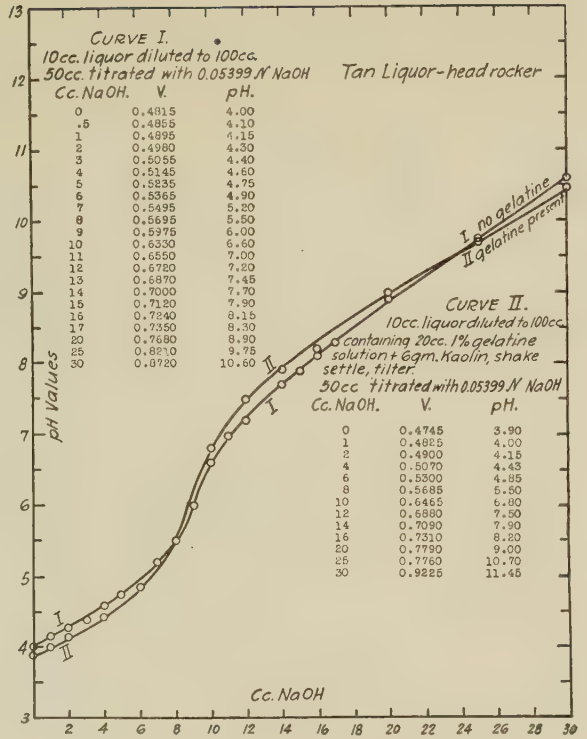
The curves for the untreated tan liquors are quite similar to that of tannic acid, there being, however, a less pronounced break than in the case of either gallic or tannic acid. An indication of a break occurs when about 8 cc. of sodium hydroxide have been added and then a more gradual decrease due to the neutralization of weaker acid substances. The very close similarity between the curves for

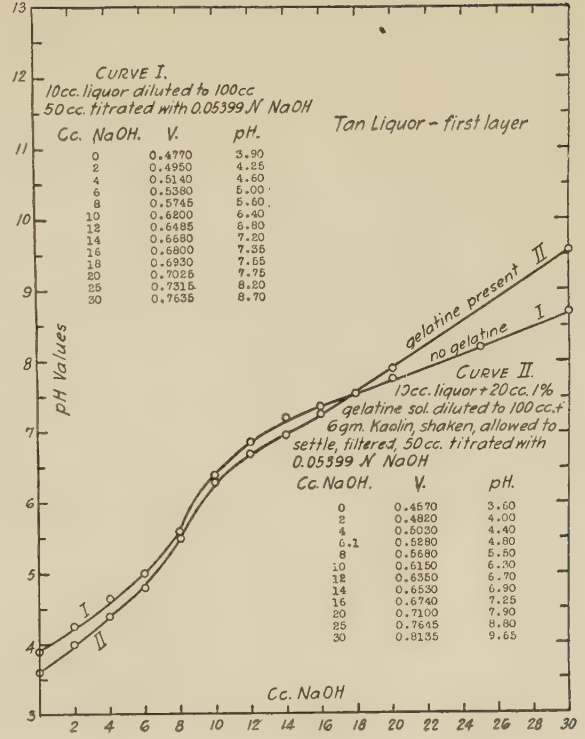


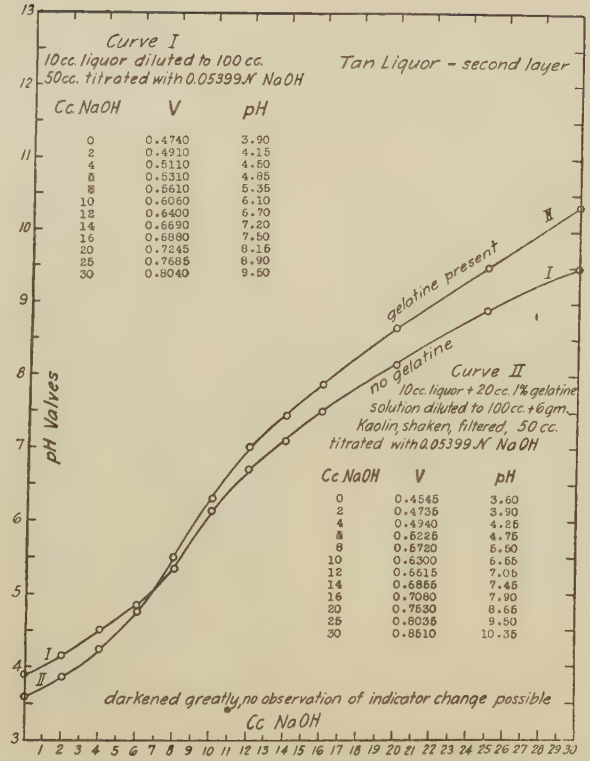
the untreated tan liquors and those from which tannins had been precipitated with gelatin is quite surprising. It shows that very few of the weakly acid substances present in the tan liquor are removed by gelatin and it seems therefore, to have been definitely established that the flattening of the gelatin precipitated tan liquor curve is due to the neutralization of weak acid substances which remain unprecipitated by the gelatin, rather than to any action of gelatin or gelatin salts with sodium hydroxide. This also then is the reason why the acidity of this solution cannot be quantitatively determined by the use of indicators.

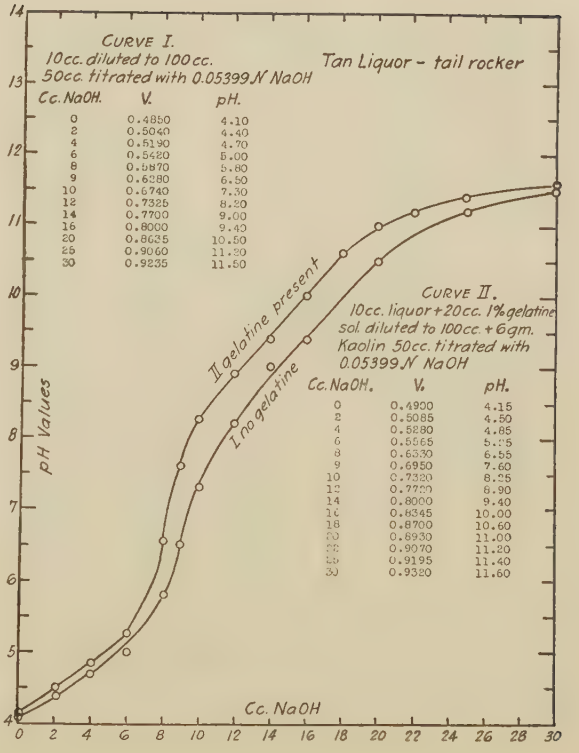

Curve I.
10cc. acid solution plus 50cc. water
Cc. NaOH. V. pH.
0 0.4260 3.05
2 0.4600 3.65
4 0.4845 4.10
6 0.5055 4.40
8 0.5330 4.85
9 0.5650 5.40
10 0.6590 7.00
12 0.7060 7.80
14 0.7400 8.40
16 0.7640 8.60
18 0.7730 8.90
20 0.7915 9.05
25 0.8200 9.75
30 0.8615 10.40
0.05399 N NaOH used
Eimer and Amend Gallic Acid
Curve I - Gallic acid alone
Curve II - Gallic acid plus gelatine
Curve II.
10cc. acid plus 50cc. water
plus 25cc. 1% gelatine solution
Cc. NaOH. V. pH.
0 0.4715 3.80
2 0.4980 4.15
4 0.5075 4.40
6 0.5280 4.85
8 0.5545 5.25
9 0.5850 5.75
10 0.6650 7.10
12 0.7235 8.15
14 0.7445 8.50
16 0.7645 8.80
18 0.7825 9.10
20 0.8080 9.60
25 0.8450 10.20
30 0.8975 11.05
no precipitate caused by gelatine
0.05399 N NaOH used
pH Values
Cc. NaOH
II
I


Data for Curve I.
Cc. NaOH. V. pH
0 0.5045 4.40
1 0.6310 6.10
2 0.6738 7.30
3 0.6900 7.55
4 0.7030 7.80
5 0.7115 7.90
6 0.7190 8.05
7 0.7260 8.15
8 0.7285 8.20
10 0.7400 8.40
12 0.7525 8.60
14 0.7650 8.80
16 0.7750 9.00
18 0.7900 9.25
20 0.8055 9.50
22 0.8175 9.70
24 0.8570 9.85
26 0.8350 10.00
28 0.8475 10.20
Curve I - 10cc. pyrogallic acid solution (25 gm. per 2 L.) plus 100cc. water
Curve II - 10cc. tannic acid solution (65 gm. per 2 L.) plus 100cc. water
Data for Curve II.
Cc. NaOH V. pH
0 0.4340 3.23
2 0.4810 4.00
4 0.5350 4.93
6 0.6085 6.17
8 0.6570 7.00
10 0.6955 7.62
12 0.7190 8.05
14 0.7310 8.22
16 0.7400 8.40
18 0.7545 8.64
20 0.7470 9.00
25 0.8175 9.70
30 0.8585 10.40
pH Values
Cc. NaOH
I
II


CURVE I.
10cc. liquor diluted to 100cc.
50cc. titrated with 0.05399 N NaOH
Tan Liquor-head rocker
Cc. NaOH. V. pH.
0 0.4815 4.00
.5 0.4855 4.10
1 0.4895 4.15
2 0.4980 4.30
3 0.5055 4.40
4 0.5145 4.60
5 0.5235 4.75
6 0.5365 4.90
7 0.5495 5.20
8 0.5695 5.50
9 0.5975 6.00
10 0.6330 6.60
11 0.6550 7.00
12 0.6720 7.20
13 0.6870 7.45
14 0.7000 7.70
15 0.7120 7.90
16 0.7240 8.15
17 0.7350 8.30
20 0.7680 8.90
25 0.8210 9.75
30 0.8720 10.60
I no gelatine
II gelatine present
CURVE II.
10cc. liquor diluted to 100cc.
containing 20cc. 1% gelatine solution + 6gm. Kaolin, shake settle, filter
50cc titrated with 0.05399 N NaOH
Cc. NaOH. V. pH.
0 0.4745 3.90
1 0.4825 4.00
2 0.4900 4.15
4 0.5070 4.43
6 0.5300 4.85
8 0.5685 5.50
10 0.6465 6.80
12 0.6880 7.50
14 0.7090 7.90
16 0.7310 8.20
20 0.7790 9.00
25 0.7760 10.70
30 0.9225 11.45
pH Values
Cc. NaOH


CURVE I.
10cc. liquor diluted to 100cc
50cc. titrated with 0.05399 N NaOH
Tan Liquor - first layer
Cc. NaOH. V. pH.
0 0.4770 3.90
2 0.4950 4.25
4 0.5140 4.60
6 0.5380 5.00
8 0.5745 5.60
10 0.6200 6.40
12 0.6485 6.80
14 0.6680 7.20
16 0.6800 7.35
18 0.6930 7.65
20 0.7025 7.75
25 0.7315 8.20
30 0.7635 8.70
gelatine present II
no gelatine I
CURVE II.
10cc. liquor + 20cc. 1% gelatine sol. diluted to 100cc. + 6gm. Kaolin, shaken, allowed to settle, filtered, 50cc. titrated with 0.05399 N NaOH
Cc. NaOH. V. pH.
0 0.4570 3.60
2 0.4820 4.00
4 0.5030 4.40
6.1 0.5280 4.80
8 0.5680 5.50
10 0.6150 6.30
12 0.6350 6.70
14 0.6530 6.90
16 0.6740 7.25
20 0.7100 7.90
25 0.7645 8.80
30 0.8135 9.65
pH Values
Cc. NaOH


Curve I
10cc. liquor diluted to 100 cc.
50cc. titrated with 0.05399 N NaOH
Tan Liquor - second layer
Cc. NaOH V pH
0 0.4740 3.90
2 0.4910 4.15
4 0.5110 4.50
6 0.5310 4.85
8 0.5610 5.35
10 0.6060 6.10
12 0.6400 6.70
14 0.6690 7.20
16 0.6880 7.50
20 0.7245 8.16
25 0.7685 8.90
30 0.8040 9.50
gelatine present
no gelatine
Curve II
10cc. liquor + 20cc. 1% gelatine solution diluted to 100cc. + 6gm. Kaolin, shaken, filtered, 50cc. titrated with 0.05399 N NaOH
Cc NaOH V pH
0 0.4545 3.60
2 0.4735 3.90
4 0.4940 4.25
6 0.5225 4.75
8 0.5720 5.50
10 0.6300 6.55
12 0.6615 7.05
14 0.6855 7.45
16 0.7080 7.90
20 0.7530 8.65
25 0.8035 9.50
30 0.8510 10.35
darkened greatly, no observation of indicator change possible
pH Values
Cc NaOH


Curve I.
10cc. diluted to 100cc.
50cc. titrated with 0.05399 N NaOH
Tan Liquor - tail rocker
Cc. NaOH. V. pH.
0 0.4850 4.10
2 0.5040 4.40
4 0.5190 4.70
6 0.5420 5.00
8 0.5870 5.80
9 0.6280 6.50
10 0.6740 7.30
12 0.7325 8.20
14 0.7700 9.00
16 0.8000 9.40
20 0.8625 10.50
25 0.9060 11.20
30 0.9235 11.50
II gelatine present
I no gelatine
Curve II.
10cc. liquor + 20cc. 1% gelatine sol. diluted to 100cc. + 6gm. Kaolin 50cc. titrated with 0.05399 N NaOH
Cc. NaOH. V. pH.
0 0.4900 4.15
2 0.5085 4.50
4 0.5280 4.85
6 0.5565 5.35
8 0.6330 6.55
9 0.6950 7.60
10 0.7320 8.25
12 0.7720 8.90
14 0.8000 9.40
16 0.8345 10.00
18 0.8700 10.60
20 0.8930 11.00
22 0.9070 11.20
25 0.9195 11.40
30 0.9320 11.60
pH Values
Cc. NaOH

The tan liquor curves given above also show quite conclusively that when tannins are precipitated with gelatin and the resultant solution titrated with $N/10$ alkali, the decrease in the concentration of hydrogen ion per unit of alkali added is, in most cases, too small to allow of an accurate titration by use of an indicator. The acidity decreases so gradually that a sharp color change is not to be expected. It was also noticed that when the tannins were precipitated with gelatin the precipitation was very incomplete. The resultant solution being frequently quite yellow in color. This error might be avoided, to some extent, if the precipitation was carried out in the presence of lower concentrations of gelatin. When weak liquors are analyzed by the official method a very large excess of gelatin is used. Proctor ("Principles of Leather Manufacture," 1922 Edition, p. 151) points out that the tannins even in very dilute solutions are all precipitated by gelatin but that this precipitate dissolves in the presence of a large excess of gelatin, which evidently acts as a protective colloid. A better procedure when using gelatin as a precipitant would be that suggested by Smoot.[27] Smoot recommends that the amount of gelatin added should vary with the percentage of tannin present. It is, however, difficult to determine when enough gelatin has been added to completely precipitate the tannins; also when an excess of gelatin is not present the precipitate settles out much more slowly.

The failure on the part of gelatin to completely precipitate the tannins has been recognized by various investigators. Reed[28] points out that it is not necessary that there should be an entire absence of tannins in the solution when titrated as they will not interfere when hematine is used as an indicator. It has been our experience that the unprecipitated tans do interfere most seriously, due to the fact that when a pH value of about 6.7 is reached the tannins turn dark brown in color just as does pyrogallic acid when its solutions are made alkaline. The color change that takes place when only small amounts of tans are present is very similar to the color change of hematine at this pH value and the writer ventures the opinion that in control work many analysts have recorded data based upon the color change of the unprecipitated tans rather than to any color change of the indicator itself. Solutions containing an amount of tans so small that they were practically colorless, gave this pronounced color change when titrated electrometrically with $N/10$ NaOH, no indicator being present, and a constant flow of hydrogen gas through the solution being maintained throughout the titration.

[27] *J. Am. Lea. Chem.*, **6**, 585 (1911).
[28] *Ibid.*, **8**, 87 (1908).

Another serious defect in the official method, due to the method of detannizing is that in many cases the final titration is carried out in the presence of a very high concentration of gelatin. Sorensen[29] long ago pointed out this protein error when he says "Most indicators combine with natural protein substances and as a result, even if the combinations are not indicated by a visible deposit, the indicator does not change color at all in most cases and hence becomes useless." In a later place in the same article after having studied the action of a great number of indicators and having determined electrometrically the conc. H^+ at which they change in the presence of proteins, he says "In the presence of large amounts of natural proteins most of the indicators are useless."

In view of the titration curves presented above and the fact that, in the official method the final titration is frequently carried out in the presence of high concentrations of gelatin, it is quite understandable why various investigators have been unable to obtain an indicator which would give a satisfactory color change. Proctor[30] used the gelatin precipitation method as outlined by Koch using azolitmin as an indicator. He states that his results were very unsatisfactory and further adds "The color change is gradual and the end point difficult to determine, so that the personal equation enters largely and concordance between observers is not usually good." Attention is called to this statement in particular as we claim to have shown that this defect is characteristic of any method which uses gelatin as a detannizing medium, quite independently of the indicator used. It seems quite clear, therefore, that some other method must be employed for detannizing the solution.

The last part of the official method to be considered is the indicator employed, namely hematine. Hematine is a very unusual indicator obtained by the extraction of logwood and subsequent oxidation and purification. In order for an indicator to be suitable for a certain titration it must show a sharp color change at the desired conc. H^+ and this color change should not extend over a considerable range of acidity. Hematine does not meet these requirements. It possesses a different color for almost every pH value from 10^{-3} to 2. Salm,[31] by use of a colorimeter with buffer solutions of known pH values has recorded the colors which he observed as follows. 2N raspberry-red, N pink, 10^{-1} green-gray, 10^{-2} greenish yellow slowly going gray, 10^{-4} green-yellow, 10^{-6} brown with a trace of red, 10^{-7} bright lilac, 10^{-8} violet, 10^{-9} red-violet, 10^{-10} red-violet turning

[29] *Comptes rendus des Travaux du Laboratoire de Carlsberg*, **8**, 59 (1909).
[30] *J. Am. Lea. Chem.*, **6**, 59 (1911).
[31] *Zeit. für Physik. Chemie*, **57**, 471 (1906).

brown, 10^{-12} dark-red-violet, 10^{-13} dark-red, later slowly brown, 10^{-14} dark-red, later brown then yellowish green, 10^{-15} blue-violet. It is interesting to note that at a conc. H^+ of 10^{-3} hematine gives a green-yellow color while at 10^{-14} it gives a yellowish green.

By observing the color changes of hematine during electrometric titrations and by use of standard solutions of KH_2PO_4 and Na_2HPO_4 in different proportions which give a range of pH values from 4.5 to 8.3, the colors given above were checked up. Not all of the colors mentioned by Salm could be distinguished without the colorimeter, a greenish yellow at 10^{-2} and 10^{-3} could easily be seen. This color changed gradually into a reddish brown at 10^{-6} and with decreasing acidity this color gradually changed to a violet which slowly darkened in color.

Although the writer has never been able to use hematine with any degree of certainty the following results are representative of data obtained in attempting to determine the pH values of the more pronounced color changes observed during a titration. 25 cc. of 0.1234 *N* acetic acid were added to 100 cc. of distilled water and titrated electrometrically with 0.08955 *N* NaOH in the presence of hematine as an indicator. Three color changes were observed which seemed more distinct than the others and although in duplicate analysis we frequently failed to check ourselves within 0.6 cc. the following are fair averages of the results obtained.

Cc. NaOH used		V		pH
0		0.4177		2.92
First end point	34.00 (Worst end point)	0.6404	(Faint violet)	6.68
Second end point	34.65 (Best end point)	0.8043	(Lilac)	9.47
Third end point	35.00 (Intermediate end point)	0.8302	(Deep violet)	9.90

The best end point of the three appeared at a pH value of 9.47 but as this is far too alkaline, the very poor end point at 6.68 must be used.

In order to determine whether or not hematine was subject to a protein error the following work was carried out. Twenty-five cc. of 0.12342 *N* acetic acid were added to a mixture of 25 cc. of neutral one per cent. gelatin solution and 75 cc. of distilled water. This solution was then titrated with 0.08955 *N* NaOH using hematine as an indicator. If the solution was allowed to stand for five minutes after the addition of the acid the yellow color of the hematine disappeared and no color developed when sodium hydroxide was added. If titrated immediately after the addition of acid

the only color change was a faint lilac when 33.40 cc. NaOH had been added, upon further addition of NaOH no further color changes were observed.

NaOH	End Point V	pH
33.40	0.6155	6.27

From the above facts it seems quite clear that hematine is an impossible indicator. Not only is it constantly changing color with changing acidities but in some cases the colors are not permanent, even when the conc. H^+ is held constant.

Proctor,[32] in discussing the use of hematine as an indicator says "While other indicators change color more or less sharply at a definite conc. H^+ hematine is practically always changing color from a conc. H^+ of twice normal to 10^{-15}, but the authors estimate that the particular color change taken as an end point took place at about 10^{-7}." Proctor presents data for six tan liquors which he says were his best results obtained when hematine was used as an indicator. For one of these liquors there is a difference in duplicate analysis of 1.20 cc. $N/10$ NaOH for a total volume of 21.40 cc. used. Proctor speaks of hematine as a very difficult indicator and states that the greatest difficulty is the extremely gradual nature of the color change; the yellow color almost imperceptibly giving rise to a yellowish pink, very difficult to distinguish from it.

Frey,[33] in relating his experience with this indicator says "It should be mentioned that none of the end points were sharp, this being true to some extent for even the blank solutions, but because of lack of experience with the indicator it cannot be stated whether or not the bewildering sequence of colors was characteristic. Practically all of the solutions darkened as the titrations progressed but it is believed that they were not carried beyond a point which might be mistaken for the end point, although working under known conditions may have exerted a sub-conscious influence."

Reed[34] furnishes further data against the use of hematine as an indicator when he states that the end point varies with the acid being titrated. Reed states that when acetic acid is being titrated with standard sodium hydroxide the end point is the appearance of a red purplish color, for lactic acid a bluish red color, and for gallic acid a red color.

A study of the official method has revealed the following facts:

1. The addition of fifteen grams of kaolin will, according to our

[32] *J. Am. Lea. Chem.*, **6**, 64 (1911).
[33] *Ibid.*, **14**, 393 (1919).
[34] *Ibid.*, **3**, 86 (1908).

results, introduce an error of about seven to eight per cent., due to the adsorption of the acids present.

2. The removal of tans with gelatin is subject to the following objections.

(*a*) The precipitation is incomplete and the tannins remaining in solution give rise to a color change during titration which is quite likely to be confused with the color change of hematine.

(*b*) The solution resulting from the precipitation of the tans is of such a nature that when it is titrated with *N* 10 alkali, the decrease in the conc. H^+ per cc. of alkali added is not great enough to allow of a satisfactory titration. No sharp color change of the indicator could be expected.

(*c*) The large amount of gelatin in solution at the time of titration will interfere with a proper color change of hematine due to what Sorensen has called "The Protein Error."

3. Hematine is not a satisfactory indicator. Its color change is not sharp and definite but is very vague and extends over a considerable range of H^+ concentrations. Also it is not sufficiently free from the protein error to be successfully used in this titration.

In view of these facts it seems quite clear that any further refining of the official method by perfection of details is wasted effort, as the method is fundamentally wrong and scientifically impossible.

Having established the defects of the official method we next attempted to build up a method of analysis in which these shortcomings are eliminated.

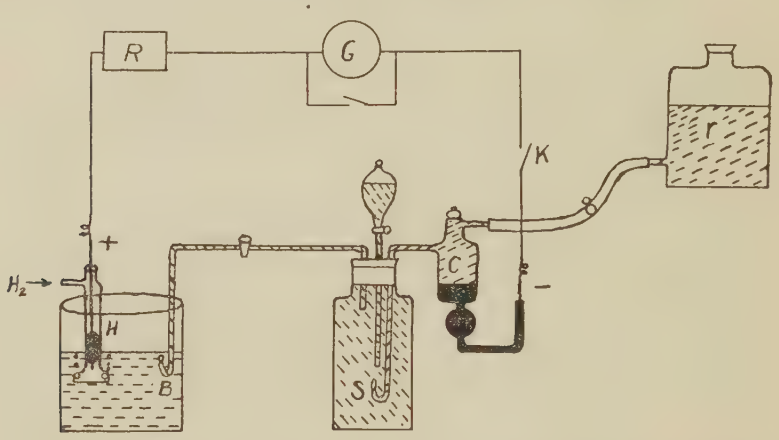
Practically every investigator who has worked on this problem has expressed the belief that no method involving detannizing can be successfully used. Proctor[35] says "A very serious objection to nearly all methods of detannizing is that certain amounts of acid are co-precipitated with the tannins—in every case of detannizing examined bodies otherwise estimated as acids are carried down with the tannins." Although our experience is not entirely in accord with this last statement we have found that whenever "these bodies otherwise estimated as tannins" are not removed in the detannizing process, the resultant solution is of such a nature that it cannot be accurately titrated by use of indicators.

It is almost imperative, therefore, that we have a method which will make possible a titration without the removal of tannins. This, of course, prohibits the use of indicators. Sand and Law[36] have presented a very satisfactory electrometric method which has been commented on in an earlier part of this article. It has never been ac-

[35] *Ibid.*, **6**, 59 (1911).
[36] *Ibid.*, **30**, 3 (1911).

cepted by leather chemists, however, due to the fact that it makes use of complicated and expensive apparatus and that a knowledge of physical chemistry is necessary for its intelligent use.

It occurred to the writer that the use of a cadmium half cell such as used by Pinkhol,[37] and Sharp and MacDougall,[38] would make possible an entirely satisfactory titration with simple apparatus, requiring less manipulative skill than an ordinary indicator titration. The apparatus used is represented by the diagram given below.



The cell marked (*c*) is a cadmium half cell containing 12% cadmium amalgam in contact with a solution of cadmium sulphate and potassium iodide. This cadmium half cell constitutes the negative pole of the cell, while the hydrogen electrode (*h*) constitutes the positive pole. When the difference of potential between these two electrodes is zero there will be no deflection of the galvanometer.

Sharp and MacDougall have presented data[38] by use of which cells of various composition can be prepared so as to give differences of potentials corresponding to a wide range of hydrogen ion concentrations. They also make use of lead amalgams with lead iodide to be used for very high concentrations of hydrogen ions. They recommend the preparation of the electrode solutions by making a two normal solution of potassium iodide and a 0.5 *N* solution of cadmium sulphate and then, by use of a table which they have developed, determine the number of cc. of these solutions which should be mixed and diluted to 100 cc. in order to prepare a solution of the concentration required for the desired pH value. This necessitates the use of

[37] *Chem. Weekblad,* **16,** 1168 (1919).
[38] *J. Am. Chem. Soc.,* **44,** 1193 (1922).

very pure and thoroughly dried chemicals. A temperature of 500° C. being used for this purpose.

A simple and quicker method of preparing these electrode solutions using undried salts of ordinary c. p. purity is as follows. Suppose we wish to prepare an electrode solution of such strength that when used with twelve per cent. cadmium amalgam and balanced against a hydrogen electrode in the above set up, the point of zero deflection of the galvanometer will register a pH value of seven in the solution bathing the hydrogen electrode. A potentiometer set up with a hydrogen electrode as the cathode and a saturated potassium chloride calomel electrode constituting the anode (H_2(1 atmos.) H^+ 10^{-7}-KCl sat., HgCl, Hg°) would give a reading of 0.6614 volt on the potentiometer. We now substitute a twelve per cent. cadmium amalgam bathed with a 0.5 N solution of cadmium sulphate for the hydrogen electrode and, having the potentiometer set at 0.6614 volt, add potassium iodide solution slowly with constant stirring until the addition of a fraction of a drop will cause no deflection of the galvanometer or a slight deflection in the opposite direction.

K is a key to make and break the circuit. G is a Leeds and Northrup No. 2285 high sensitivity galvanometer. R is resistance to protect the galvanometer. H is a Hildebrand type of hydrogen electrode. S is a saturated potassium chloride salt bridge to reduce contact potentials and r is a large reservoir of the electrode solution which is being used in the cadmium half cell.

The type of cell shown above for the cadmium half cell is especially useful. It can be completely filled and kept so with little difficulty. This is quite essential as the electrode solution being used is not a saturated solution and the possibility of an error due to evaporation must be guarded against. The side arm of the cadmium half cell should be removed from the salt bridge each day and a little of the electrode solution run from the reservoir through the cell, in order to guard against diffusion of the potassium chloride into it. A cadmium sulphate and potassium iodide solution kept in this way gave practically the same voltage for several months.

The operation of the set-up is so simple that it needs little comment. The diluted tan liquor to be titrated is placed in beaker B with the hydrogen electrode as indicated in the above diagram. Standard alkali is then run in until one drop causes a deflection of the galvanometer in the opposite direction thus clearly indicating the end point of the titration.

When a strong acid is being titrated with a strong base, the addition of one drop of $N/20$ NaOH at the end point will cause a wide deflection of the galvanometer in the opposite direction. When very

weak acids are titrated, as in the case of a tan liquor, the falling off of the galvanometer deflections is very gradual and at the end point a very slight movement in the opposite direction is caused by the addition of one drop of the alkali. The end point obtained, however, is very accurate, as the slightest motion of the galvanometer is easily detected by the eye, whereas the color change of the indicator that would result from the slightly decreased conc. H^+ could not be easily detected. Thus when working with very weak acids, even in colorless solutions, the use of the cadmium half cell is preferable and affords a much more accurate method of titration than does the use of indicators.

The accuracy of the set-up was established by several different methods. Diluted solutions of acetic, lactic, butyric and propionic acids, containing two drops of phenolphthalein, were titrated separately with $N/20$ sodium hydroxide. In every case the same drop of alkali that caused the galvanometer to swing from the right to the left also caused the appearance of a faint pink color in the solution being titrated. In the same way mixtures of the above acids were titrated using phenolphthalein and phenol red as indicators, the galvanometer and indicator end points agreeing in each case.

The method was further tested by titrating ten different tan liquors as follows. Ten cc. of the untreated liquor were diluted to 100 cc. and titrated by use of the cadmium half cell with 0.08955 N sodium hydroxide as before.

To 10 cc. portions of each of the above tan liquors definite amounts of an 0.04535 N solution of mixed acids were added, diluted to 100 cc. and the titration by use of the cadmium half cell repeated with 0.08955 N NaOH. Phenol Red was used as the indicator in the standardization of the acid and base used. The relationship between the cc. of acid added and the cc. of standard NaOH necessary to neutralize it are given below.

Liquor No.	I Cc. 0.08955 N NaOH Used in Original Titration. No Acid Added	II Cc. 0.04535 N Acid Added to 10 cc Original Liquor	III Cc. 0.08955 N NaOH Used in Final Titration
1	11.80	15	19.32
2	12.15	10	17.11
3	9.10	25	21.71
4	6.35	25	18.99
5	14.75	15	22.27
6	20.80	10	25.81
7	12.50	15	20.10
8	11.55	15	19.07
9	13.00	10	18.00
10	12.75	25	25.35

Liquor No.	IV or (III-I) Cc. 0.08955 *N* NaOH Required for Added Acid.	V Cc. NaOH Necessary for Added Acid Calculated to 0.04535 *N*	VI Difference in Volume of 0.04535 *N* Acid Added and Found
1	7.52	14.85	−0.15 cc.
2	4.96	9.80	−0.20 cc.
3	12.61	24.90	−0.10 cc.
4	12.64	24.95	−0.05 cc.
5	7.52	14.85	−0.15 cc.
6	5.01	9.90	−0.10 cc.
7	7.60	15.00	0.00 cc.
8	7.52	14.85	−0.15 cc.
9	5.00	9.85	−0.15 cc.
10	12.60	24.85	−0.15 cc.

By a reference to Column VI it is seen that very good results were obtained by the use of this method, the errors in each case being very small as compared with the differences of 0.5 cc. to 0.8 cc. or more which are likely to result when the official method is used.

SUMMARY

It has been shown that the official method of the A. L. C. A., for the determination of the acidity of tan liquors is not good for the following reasons.

I. The addition of kaolin to clarify the solution introduces a considerable error due to adsorption.

II. The indicator used, *viz.*, hematine, is very unsatisfactory, giving very poor color changes and being subject to a very large protein error.

III. Gelatin gives a very incomplete precipitation of the tannins and the solution resulting is of such a nature that its acidity cannot be determined by the use of indicators. The decrease in the conc. H^+ per unit of alkali added being too small to give sharp color changes of the indicator.

A simple accurate method employing the cadmium half cell has been presented. This method is well suited for a control method as it can be generally applied, is quite accurate and can be used with a diluted solution of the untreated liquor; a colored or opaque solution offering no interference. This method is also easily used, the skill required for conc. H^+ determinations being unnecessary. It can also be handled by different analysts with the same degree of accuracy, as the personal equation has been eliminated. The slight movement of the galvanometer indicating the end point can be clearly seen by all whereas the ability to detect very slight color changes varies greatly in different individuals.

There seems to be no good reason why this method should not be accepted and generally used as a control method.

VITA

Ernest Little was born at Johnstown, Fulton County, New York, June 9, 1888. He attended the elementary school at Johnstown, New York, and received his secondary education at the Johnstown High School, from which he was graduated in 1907. He received a Bachelor of Science degree in chemistry from the University of Rochester in 1911. From 1911 to 1914 he studied and taught chemistry at the University of Rochester, where the degree of M.S. was received in 1913. From 1914 to 1919 he was instructor in leather chemistry at Pratt Institute, Brooklyn, New York. During this period graduate work was pursued at Columbia University and in 1919 he was awarded the degree of M.A. by this University.

Since 1919 he has been a member of the chemistry staff at Rutgers College and in 1920 was made Associate Professor of Chemistry at that institution. He was previously assistant in physics and mathematics at Mechanics Institute Rochester, New York. He has taught four summer sessions in the chemistry department of Columbia University, and one summer session at Adelphi College, Brooklyn. Since 1920 he has also been Professor of Chemistry and Physics at the New Jersey College of Pharmacy, Newark, New Jersey.

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